

Controls on Bioavailability of Phosphorus in the Coastal Ocean: A Coupled Geochemical and Enzymatic Approach

Kathleen C. Ruttenberg
Department of Marine Chemistry and Geochemistry
McLean Laboratory, MS#8
Woods Hole Oceanographic Institution
Woods Hole, MA 02543
phone: (508)457-2482 fax: (508)457-2183 email: kruttenberg@whoi.edu
Award #: N00014-95-1-0478
http://www.onr.navy.mil/sci_tech/ocean/onrpgahj.htm

LONG-TERM GOAL

My long term goal is to identify the processes which control the supply of bioavailable nutrients to the coastal ocean and to evaluate controls on nutrient limitation of biological productivity in the coastal ocean. Of particular interest to me is the possibility that nutrients other than nitrogen can limit biological productivity, and understanding the conditions which favor limitation by phosphorus.

OBJECTIVES

I have two broad objectives. The first is to quantify and characterize the different nutrient sources to the coastal field area, the Eel River Shelf, on a seasonal basis. The external nutrient sources include riverine input, benthic flux, and upwelling. Bioavailable forms of nutrients are distinguished from unavailable forms using geochemical methods. The second objective is to link the bioavailable nutrient supply to the metabolic nutrient demand expressed by phytoplankton. Finally, the seasonal presence of nutrient limitation is determined, as is the identity of the limiting nutrient(s).

APPROACH

I participated in three cruises to the Eel River Shelf: May 1996, July 1996, and January 1997. I conducted hydrographic surveys of the shelf consisting of 3 to 5 shore-perpendicular transect lines, 5 to 8 stations per transect. The core of the sampling grid was between 30 and 70 m water depth, with stations every 10 meters. Deeper stations were sampled less regularly in order to characterize the deep source of potentially upwelled water. At each station a CTD (with fluorometer, transmissometer, oxygen probe, and PAR sensor) and niske rosette were deployed, and water collected at 3 to 5 water depths per station. Typically I collected samples from approximately 100 water column depth intervals per cruise. Water samples were filtered through 0.40 μ m polycarbonate filters for dissolved nutrient analyses and collection of particulates for phosphorus speciation, through GF/F filters for DOC and DON analysis, for enzymatic (alkaline phosphatase: APase) assays of the particulates, elemental (CHNS) analysis, and chl-a determinations.

I collected samples from the three main rivers draining into the Eel River Shelf (the Eel, Mad, and Van Duzen Rivers) immediately after completing each cruise. Depth integrated samples were taken at USGS river gauging stations with the help of the Eureka USGS office. Samples were processed as described above for hydrographic survey samples.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 1998		2. REPORT TYPE		3. DATES COVERED 00-00-1998 to 00-00-1998	
4. TITLE AND SUBTITLE Controls on Bioavailability of Phosphorus in the Coastal Ocean: A Coupled Geochemical and Enzymatic Approach				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Woods Hole Oceanographic Institution, Department of Marine Chemistry and Geochemistry, Woods Hole, MA, 02543				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002252.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

I use a variety of geochemical methods to distinguish bioavailable from unavailable forms of nutrients (Ruttenberg 1992; Monaghan and Ruttenberg 1998). Standard methods are used for chl-a determinations. Working with one of my students, I have modified the methylumbelliferyl APase assay (Hoppe 1983) for use on a Cytofluor, which permits significantly more rapid sample throughput than is possible with the traditional mode of measurement using a fluorometer.

Using APase as an indicator of phosphorus limitation, in conjunction with determination of nutrient inventories and biomass in the water column, the nutrient limitation status of the Eel River Shelf coastal system can be evaluated.

WORK COMPLETED

The suite of three seasonal cruises has been successfully completed and all analyses of dissolved constituents are completed. Analysis of particulates is nearly completed. Interpretation of the dissolved inorganic nutrient inventories is well underway, dissolved organic nutrient data are in hand and ready to be integrated into the overall data synthesis.

Rapid-response samples collected via helicopter immediately after the peak of the Eel River floods of 1997 and 1998, as well as surface sediment samples collected from a small vessel soon after the floods, were collected for us by other ONR-funded scientists. Processing of these samples has been completed and analyses are underway.

Working with my research assistant and student, I completed the analytical work developing and verifying methods for quantifying dissolved organic phosphorus (DOP) and APase activity. The DOP manuscript has been accepted for publication in *Limnol. Oceanogr.*, and I anticipate that a second manuscript on the APase cytofluor method will be ready for submission early in 1999.

Two abstracts have been published for national meetings, one paper has been accepted for publication, and an article featuring this my work on the Eel River Shelf has been published in the Woods Hole Oceanographic Institution 1997 Annual Report. Additional manuscripts and abstracts published with support from this grant, not focussed on the Eel River Shelf, are also listed below.

RESULTS

Seasonal variability in the nutrient inventories and profile shapes are evident in results from the three STRATAFORM cruises. Dissolved Organic Phosphorus (DOP) constitutes an important fraction of the total dissolved phosphorus inventory in both spring and summer. However, there are important seasonal differences. In the spring, Dissolved Inorganic Phosphorus (DIP) concentrations typically exceed DOP concentrations throughout the water column. Summer profiles, in contrast, show surface water DOP concentrations as much as six times higher than DIP concentrations. These DOP concentration maxima typically coincide with a maximum in chl-a, DIP concentrations near detection limits, and the presence of alkaline phosphatase (APase) activity. The presence of APase activity, an inducible enzyme in algae and bacteria whose presence indicates phosphate limitation, suggests that algae are hydrolyzing DOP to form DIP in order to satisfy their nutritional phosphate demand. The same stations which in summer display higher DOP than DIP and high chl-a often show high surface water ammonia concentrations, as well, resulting in ratios of Dissolved Inorganic Nitrogen (DIN) to DIP (e.g. DIN:DIP) which exceed the Redfield Ratio, also consistent with a seasonally phosphate-limited system.

Plots of water column dissolved inorganic nitrogen (DIN) versus DIP indicate a shift from N-limitation in spring to P-limitation in summer, or possibly co-limitation by P and N. This trend is not evident if nitrate only is plotted against DIP (e.g. nitrate versus DIP), demonstrating the importance of including all inorganic nitrogen species in the assessment of nutrient limitation. Ammonia concentrations, in particular, are very high in the summer and drive the system toward phosphate limitation. The relationship between DIN and DIP in these nutrient/nutrient plots is tighter (higher R^2) in spring than in summer. Data from our benthic flux cores indicates that this may be due to the presence of a significant benthic phosphate flux out of sediments in summer.

Results from the January cruise show considerably lower chl-a and higher and more invariant oxygen concentrations, consistent with a lower productivity regime. The water was considerably more turbid than in spring and summer due to the recent flooding of adjacent rivers. Water column DIP concentrations from these winter-time samples are remarkably invariant, which may result from the 'phosphate buffering' effect, that is, the sorptive interaction of phosphate with terrigenous particulate matter in the water column.

IMPACT/APPLICATION

Results from the work completed to date suggest that nutrient limitation shifted from Nitrogen (N)-limited in spring to Phosphate (P)-limited in summer on the Eel River Shelf. If this kind of shift is a regular phenomenon in this coastal system, it indicates that current models of nutrient forcing on biological productivity in the coastal ocean may require radical revision. Current models assume ubiquitous N-limitation, and often focus exclusively on nitrate, only one of the possible dissolved and bioavailable species of N. This work demonstrates the necessity of including all forms of bioavailable nutrients when making an assessment of nutrient limitation of biological productivity.

TRANSITIONS

The uncertainty which exists about which nutrient is 'the' limiting nutrient precludes construction of realistic descriptive or predictive models of coastal ocean biomass dynamics. This has important implications for academic and Naval objectives centered around prediction of biogenic particle production in the coastal ocean. A major objective of this research is to provide evidence of the importance of including 'non-traditional' nutrient pools into productivity-prediction models, and to underline the importance of explicitly documenting the identity of limiting nutrients in a given ecosystem in order to avoid assumptions which may prove unrealistic.

RELATED PROJECTS

This project has benefitted greatly from the opportunity to collaborate with scientists in the ONR-funded STRATAFORM project. In particular, Chuck Nittrouer has been exceedingly helpful in accommodating ship-time needs for carrying out the work described in this report. Nittrouer and other STRATAFORM scientists have expressed interest in the water column data which I am generating as part of this project, as it will help them to constrain the sediment delivery term for strata formation on the Eel River Shelf. In addition, I have been looking at the geochemistry of surface sediments, in particular at components derived from water column productivity, to link surface sediment parameters which provide an indication of organic matter source and reactivity (chl-a, organic C:N:P ratios) to water column profiles of these same parameters. This will provide insight into the seasonal delivery of

metabolizable organic matter to the sea bed on the Eel River Shelf. The delivery of water column biogenic particulate matter (e.g. productivity) to the sea bed has a direct effect on strata preservation, through direct sedimentation, and by increasing the supply of reactive organic matter which fuels benthic bioturbating organisms, and promotes sediment reworking and destruction of strata-boundaries.

The work done to develop/verify a method for quantifying DOP in seawater is being applied to samples collected for my NSF-funded project on nutrient biogeochemistry in the lower Mississippi and Atchafalaya Rivers, and the coastal Gulf of Mexico.

REFERENCES

Hoppe, H.G. (1983). Significance of exoenzymatic activities in the ecology of brackish water: measurements by means of methylumbelliferyl-substrates. *Mar. Ecol. Progr. Ser.* 11: 299-308.

Monaghan, E. and Ruttenberg, K.C. (1998). Measurement of total dissolved phosphorus in the coastal ocean: A reassessment of available methods and an examination of seasonal water column phosphorus profiles from the Eel River Shelf. Accepted for publication 9/98, in revision.

Ruttenberg, K.C. (1992). Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* 37: 1460-1482.

PUBLICATIONS

Bauer, J.E., Ruttenberg, K.C., Wolgast, D.M., and Schrope, M. (1996). Dissolved and colloidal nitrogen and phosphorus isolated from seawater using different ultrafiltration technologies. *Marine Chemistry* 55: 33-52.

Macdonald, R.W., Ruttenberg, K.C., and Gobeil, C. (1998). The Mackenzie Shelf - Budgets and Problems. pp 63-65. In: *Proceedings of the International Workshop on Exchange Processes Between the Arctic Shelves and Basins*, Yokohama, 17-19 Feb, 1998.

Mayer, L., Keil, R., Macko, S., Joye, S., Ruttenberg, K., and Aller, R. (1998). The importance of suspended particulates in riverine delivery of bioavailable nitrogen to coastal zones. (EOS) *Trans. Amer. Geophys. Union.* 79(1): OS124.

Mayer, L., Joye, M., Keil, R., Ruttenberg, K. and Aller, R. (1998). The Importance of Suspended Particulates in Riverine Delivery of Bioavailable Nitrogen to Coastal Zones. *Global Biogeochem. Cycles.* (accepted for publication 7/98).

Monaghan, E. and Ruttenberg, K.C. (1998). Measurement of total dissolved phosphorus in the coastal ocean: A reassessment of available methods and an examination of seasonal water column phosphorus profiles from the Eel River Shelf. Accepted for publication 9/98, in revision.

Reimers, C.E., Ruttenberg, K.C., Canfield, D.E., Christiansen, M.B., and Martin, J.B. (1996). Pore water pH and the earliest diagenesis of the Santa Barbara Basin. *Geochim. Cosmochim. Acta.* 60(21): 4037-4058.

Ruttenberg, K.C., Monaghan, E. and Keon, N. Seasonal importance of dissolved organic phosphorus as a nutrient-P source in a coastal marine system: The Eel River Shelf. Submitted 9/98 for Feb. 1999 ASLO meeting.

Ruttenberg, K.C., Monaghan, E. and Keon, N. (1998). Seasonal cycle of dissolved organic phosphorus in a coastal marine system: The Eel River Shelf. (EOS) Trans. Amer. Geophys. Union. 79(1): OS52.

Ruttenberg, K.C.. (1998). New evidence for phosphorus limitation in the coastal ocean. Woods Hole Oceanographic Institution 1997 Annual Report, pp. 19-20.

Ruttenberg, K.C. and Goñi, M.A. (1997a). Phosphorus distribution, elemental ratios, and stable carbon isotopic composition of arctic, temperate, and tropical coastal sediments: Tools for characterizing bulk sedimentary organic matter. Marine Geology 139(1/4): 123-145.

Ruttenberg, K.C. and Goñi, M.A. (1997b). Depth trends in phosphorus distribution and C:N:P ratios of organic matter in Amazon Fan sediments: Indices of organic matter source and burial history. Proceedings of the Ocean Drilling Program: Scientific Results (vol. 155): 505-517.